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April 13, 1972 - November 10, 1972

FINAL REPORT

INVESTIGATIVE STUDY

of

HOLOGRAPHIC RECORDING MATERIALS DEVELOPMENT

NASA Contract NAS1-11466
Request No. 1-18-2566

Prepared For: CASE FILE COPY

NASA-Langley Research Center
Hampton, Virginia 23365

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ABSTRACT

This contract has investigated the potential of certain cis-
trans isomers and doped $LiNbO_3$ for the holographic read/write/erase
memory application. The cis-trans work involved the photochemical in-
vestigation of a number of potential materials as well as specific
molecular engineering efforts on α-methylstilbene and its derivatives.
These efforts resulted in an increase in the change in index of refrac-
tion, and thereby, in potential recording utility, of an order of
magnitude.

The work on $LiNbO_3$ was directed toward a preliminary investi-
gation of the dynamics of the writing process. Several samples and a
variety of writing conditions were investigated. An unexpected and as
yet unexplained improvement in material behavior with continued re-
cycling was observed. In addition, some effort was devoted to an analysis
of the physical conditions under which several current theories of the
"optical damage" process are valid.

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INTRODUCTION

Background

The present program is devoted to the development of materials suitable for use in high-speed, high-capacity holographic computer memories. Two classes of optical read/write/erase materials have been studied, cis-trans isomers and ferroelectrics. The rationale for this choice of materials was established under a previous study done by Battelle-Columbus Laboratories under subcontract to Radiation, Inc., under NASA Contract No. NAS8-26672 which was funded by NASA-MSFC. These studies were directed toward the identification of those classes of material which had the potential of being developed to the point of utility in the MSFC system. Due to the high-bit density required, multiple hologram recording was indicated. This, in turn, dictated the use of thick-phase holograms. The present work was carried out with an awareness of the MSFC requirements, although the MSFC system is not the sole motivation for advancing the state of the art of optical memory materials.

Summary

During the contract period, Battelle-Columbus has investigated the potential of certain cis-trans isomers and doped $LiNbO_3$ for the holographic read/write/erase memory application. The cis-trans work involved the photochemical investigation of a number of potential materials as well as specific molecular engineering efforts on α-methylstilbene and its derivatives. These efforts resulted in an increase in Δn, and thereby in potential recording utility, of an order of magnitude.

The work on $LiNbO_3$ was directed toward a preliminary investigation of the dynamics of the writing process. Several samples and a variety of writing conditions were investigated. An unexpected and as yet unexplained improvement in material behavior with continued recycling was observed. In addition, some effort was devoted to an analysis of the physical conditions under which several current theories of the "optical damage" process are valid.

Recommendations

The research on the use of cis-trans isomers of stilbene during the past 12 months has indicated that such a system may prove ideal for high-speed, high-capacity holographic memories. The substantial progress achieved, in spite of the fact that some significant technical details have not as yet been investigated, suggest that the proposed system requirements can be met. During this program an order of magnitude improvement in sensitivity has been realized, so that useful sensitivities are being approached. Thus, we recommend that in light of these advances research with cis-trans isomers be continued at Battelle-Columbus.

In the realm of inorganic, erasable phase materials, $LiNbO_3$ is clearly the most promising compound. However, several problems still exist, most notably its lack of sensitivity. Continued work should be done on the ferroelectrics to better understand the writing mechanism and to develop materials with characteristics tailored for specific applications.

CIS-TRANS SYSTEM

Organic cis-trans isomer pairs were selected for development into a holographic system by virtue of anticipated differences in the refractive indicies of the isomers. Furthermore, it was expected that the magnitude of this difference could be adjusted through molecular engineering. This expectation has been confirmed experimentally. The original choice of α-methylstilbene for examination in the present application was based on the fact that procedures for preparation of each isomer in relatively high isomeric purity were known and that sensitizers for the isomerization from each to the other were available. The lack of sufficient refractive index difference between the two unsubstituted α-methylstilbenes, which in other respects appeared satisfactory, led to selection of para-substituted stilbenes as likely candidates. Polar substituents and extended conjugation increase refractive index. The following tabulation will serve to illustrate the rationale.

I	Benzene	1.5011	(20°C)
II	Nitrobenzene	1.5524	(20°C)
III	Anisole	1.5173	(20.6°C)
IV	p-Nitroanisole	1.5707	(60°C)
V	Biphenyl	1.5882	(77.1°C)

I

II

III

IV

V
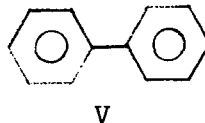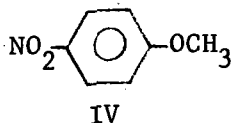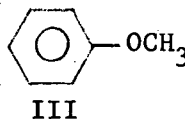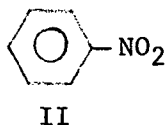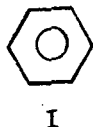
Polar substituents increase refractive index (compare II and III with I) and

are additive (IV is greater than II or III). Extended conjugation also increases

refractive index (compare V with I). Part of this change is due to density in-

creases, but part can be attributed to electronic factors. In non-planer cis-

compounds the extension of conjugation is much more limited than in trans-

compounds which are planar. Therefore, conversion of a cis- to a trans-isomer

should result in markedly increased refractive index. This effect should be

most notable, among the compounds we have already prepared, in 4-methoxy-4'-

nitro-α-methylstilbene where a change from trans- to cis- breaks the extended

conjugation of two aryl components chosen to maximize the total molecular polar-

izability of the trans-isomer. The result of this procedure is to increase the

difference in polarizability and therefore the difference in index of refraction

between the two isomers.

Synthesis

To date the following stilbenes have been prepared for evaluation.

1. <u>trans-4-Nitrostilbene</u> The reaction of p-nitrobenzenediazonium

chloride with styrene (Meerwein reaction) produced a poor yield of 1-chloro-1-

phenyl-2-p-nitrophenylethane (mp 87-88°), which upon heating overnight in reflux-

ing benzene in the presence of silica gel dehydrochlorinated to give about 60%

of trans-4-nitrostilbene, mp 154 - 157 C as yellow needles from ethanol. The

intermediate chloro compound was isolated from a tarry reaction mixture after

steam distillation removal of contaminants by first allowing crystals to form

on cooling the mass in petroleum ether, separating the crystalline mass and re-

crystallizing from petroleum ether, then from ethanol. The crude was then

chromatographed on an alumina column using ether/benzene (90/10) for elution and

the intermediate product recrystallized again from ethanol. The final product

was easily purified by recrystallization from ethanol.

2. <u>trans-4'-Nitro-α-methylstilbene</u> Similarly, the reaction of p-nitro-benzenediazonium chloride with α-methylstilbene produced a slightly higher yield of trans-4'-nitro-α-methylstilbene, yellow needles from ethanol, mp 106-108 C. No intermediate chloro compound was isolated in this case, however, and the de-hydrochlorination must have occurred spontaneously on formation of the product or during isolation. The product was isolated by first removing acetone and by-products by steam distillation, then extracting product from the residue with chloroform. The chloroform was evaporated and crude product was obtained by treating the residue with petroleum ether to separate the stilbene from tars. Recrystallizations from petroleum ether and from ethanol were not adequate to produce a product of good purity, which, however, was finally obtained by chrom-atographic separation on a column of alumina using ether/benzene (90/10) for elution. The proudct was finally recrystallized from ethanol.

3. <u>cis- and trans-4'-Methoxy-α-methylstilbene</u> The Meerwein reaction of p-methoxybenzenediazonium chloride with α--methylstyrene produces 4'-methoxy-α-methylstilbene. Work up in this case was performed by vacuum distillation of the entire crude product after removal of acetone and volatile by-products by steam distillation. The distillate, the bulk of which was collected in the range of 118-129 C at 0.2-0.25 mm, consisted of a liquid and a crystalline phase.

The solid phase was separated by filtration and crystallized from ethanol to give a very pale yellow product. The color was completely removed chromatographically using the system described above for 1 and 2, and the final product consisted of long white needles, mp 83.5-84.5 C. Only color, not melting point, had been improved by chromatography.

The liquid phase was similarly purified chromatographically to give a clear colorless liquid product. On standing, however, solid slowly deposited

from the liquid and could be removed by filtration. On further standing, more solid formed even at temperatures below $0°$ where the liquid product itself had solidified. This solid proved to be identical in melting point and mixed melting point with the solid compound first isolated. The liquid phase, with solid removed by filtration, appears on NMR examination to contain more than one compound. It can be expected to be saturated with the solid material, identified as trans-4'-methoxy-α-methylstilbene, but contains other contaminants as well. It appears that at least the bulk of the liquid product is the cis-isomer which isomerizes even in the solid state, cold and in the dark to the trans. The cis-isomer would, of course, be expected to be low melting. Whether in this particular synthesis both cis- and trans-compounds are formed or whether isomerization takes place during distillation, is not known. Literature reference to Meerwein reactions of this type cite the isolation of only one product and its configuration is not stated.

4. <u>trans-4-Methoxy-4'-nitro-α-methylstilbene</u> The starting compound, p-methoxy-α-methylstyrene, was prepared by the reaction of p-methoxyphenylmagnesium bromide (prepared from p-anisyl bromide and magnesium) with acetone and dehydration of the intermediate carbinol by distillation. Reaction of p-methoxy-α-methylstyrene with p-nitrobenzenediazonium chloride in the Meerwein reaction followed by the usual steps of steam distillation, recrystallization from petroleum ether and from ethanol and final purification by column chromatography on alumina produced trans-4-methoxy-4'-nitro-α-methylstilbene, yellow needles, mp 109-111$°$ from ethanol, in better yield than any of the preceding preparations. When, however, the steam distillation was followed by a vacuum distillation instead of recrystallization, a mixture of isomers was obtained, approximately 45% cis and 55% trans, which were separated somewhat during distillation, but not enough to give pure materials.

5. <u>Attempted preparation of 1,4-bis[β-methylstyryl]benzene</u>   In an

effort to obtain a compound with more extended conjugation, the reaction of p-

diisopropenylbenzene with benzenediazonium chloride was attempted. The former

compound was prepared from available 1,4-bis[α-hydroxyisopropyl]benzene by dehy-

dration in the presence of a trace of iodine in boiling xylene. Unfortunately,

use of the isolation techniques developed for the compounds described above did

not yield recognizable amounts of the desired compound in a single attempt with

this preparation. This result is perhaps not surprising since the Meerwein

Reaction is not a high yield preparation and this material requires reaction of

two moles of diazonium salt with a diolefin. The product would be of interest,

however, since it could exist in three, rather than two, isomeric forms (cis,

cis; cis, trans; and trans,trans) and renewed attempts to prepare it may be under-

taken in the future.

Isolation of Pure Isomers

Six techniques have been evaluated for the separation of a mixture of

cis and trans isomers, fractional crystallization, distillation, thin layer

chromatography, conventional liquid chromatography, gel permeation chromatography

and high-pressure liquid chromatography. All but the last method did not prove

fruitful. cis- and trans-4-Methoxy-4'-nitro-α-methylstilbene have been separated

by high pressure liquid chromatography, however, as shown in Figure I, peaks II

and III thought to be the two isomers, while peak I is an impurity. While to date,

only analytical size samples (microgram) have been separated, no major difficulties

are anticipated in performing preparative separations once an appropriately

larger column is made.

FIGURE I

High-pressure liquid chromatography
of cis- and trans-4-methoxy-4'-nitro-γ-methylstilbene
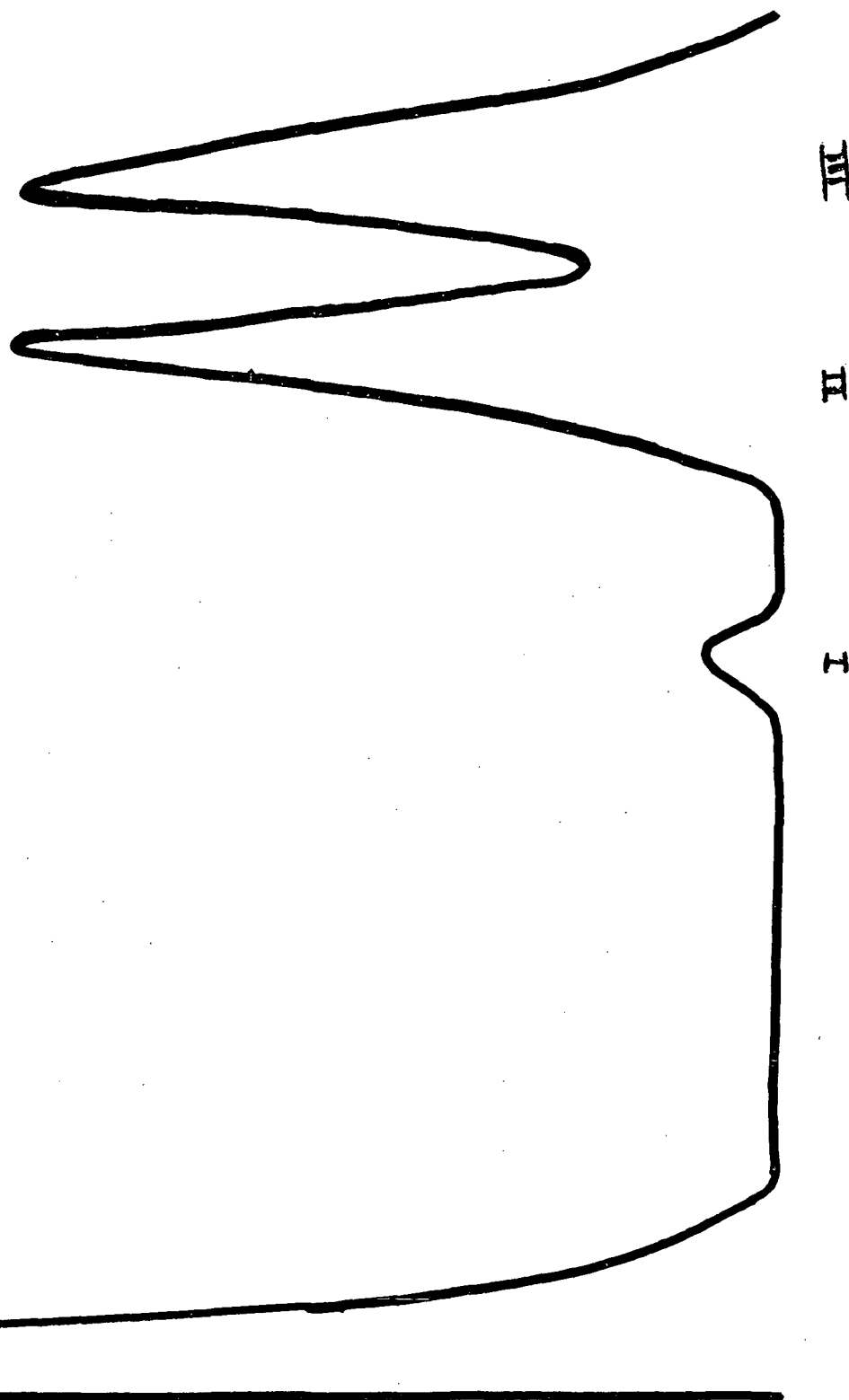
Analysis

Once the stilbenes have been prepared they naturally must be analyzed to determine whether they are cis or trans. Such a procedure is also required for the determination of isomer ratios after photolytic interconversion. Although the preliminary work reported previously utilized nuclear magnetic resonance spectroscopy (NMR), we considered three analytical techniques. These are NMR, gas chromatography, and gel permeation chromatography. Of these three, NMR has been extensively utilized, and gas chromatography and gel permeation chromatography were discarded after preliminary investigation. The pros and cons and a brief description of each technique follow.

NMR. The NMR spectra of the reaction mixtures, free of solvents, were measured at 60 MHz in deuterochloroform or deuterobenzene solution (1 - 20% w/v) using internal tetramethylsilane as the reference. The ratio of the areas of the methyl doublets (130 Hz, 2.16δ, cis; 135 Hz 2.25δ, trans) was determined from the average of 10 integrations. The precision was $\pm$ 0.2%. Disadvantages of this technique are the interferences that may occur as a result of the reaction system used.

The methoxyl groups of 4-methoxy-4'-nitro-α-methylstilbene appear in a unique position on the spectra and will most likely not be subject to interferences from other materials. Figure II represents the NMR of trans-4-methoxy-4'-nitro-α-methylstilbene; Figure III represents the NMR of a mixture of cis and trans.

Gas Chromatography. Initial studies using both flame ionization and thermal conductivity GC systems have shown that the cis- and trans-α-methylstilbene isomers are readily separable. Typical conditions were 6 ft. x 1/8 in. column packed with 3% OV-17 on chrom W with a He flow of 30 ml/min programmed from

FIGURE II. NMR Spectra (60 MHz) of 4'-Nitro-4-Methoxy-α-Methylstilbene (Trans isomer)

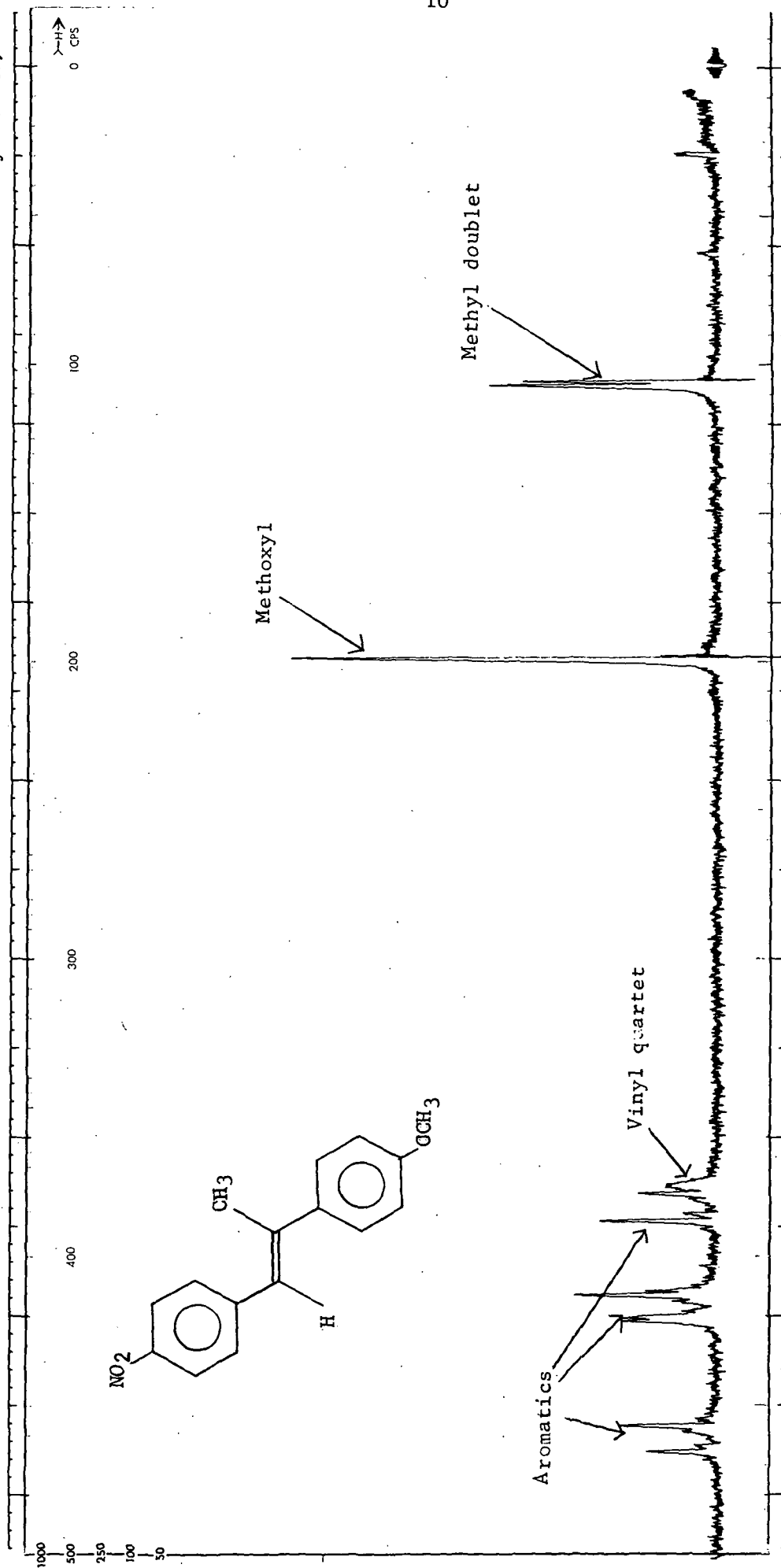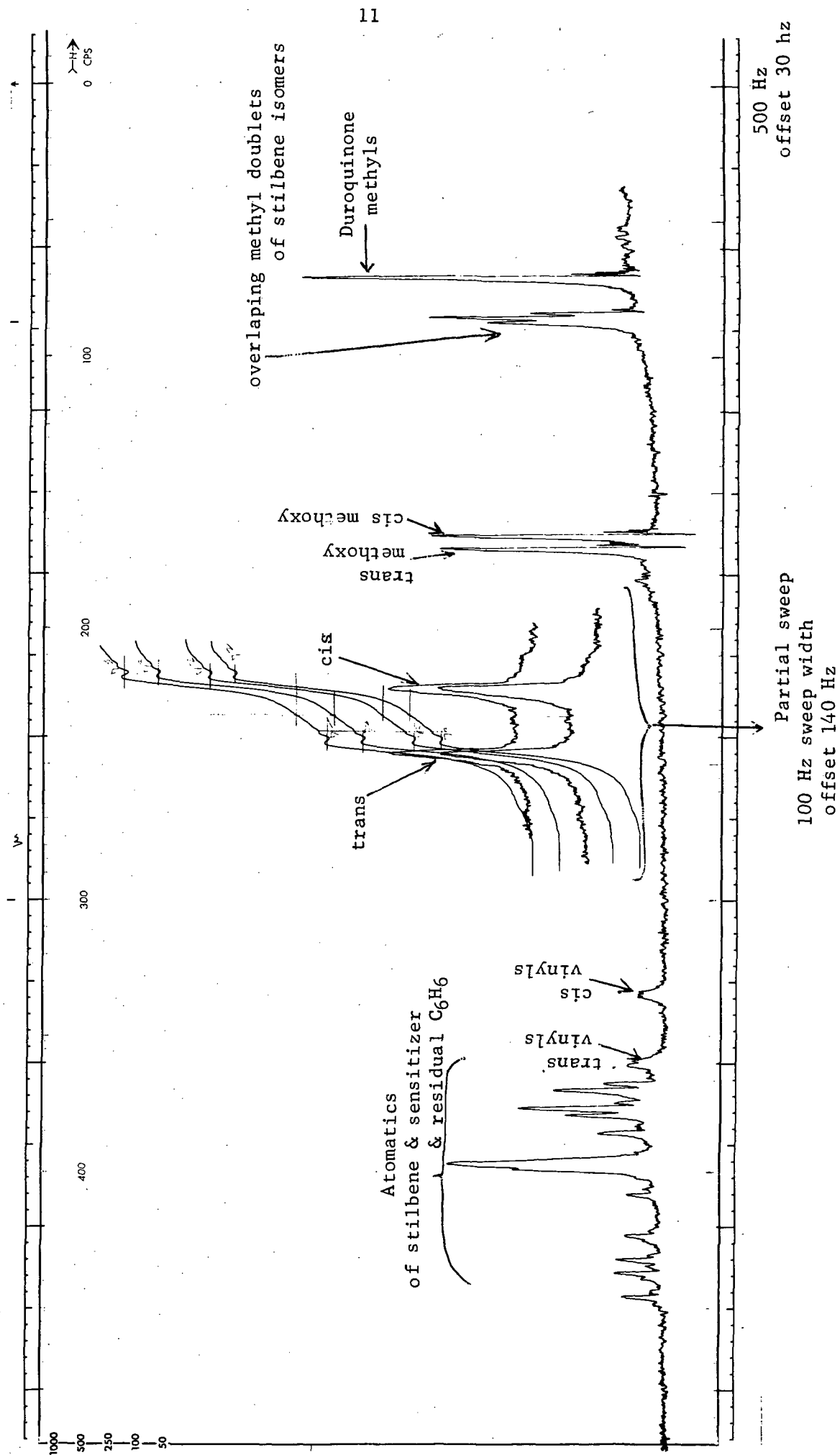Solvent:C₆D₆ 98 atom % D
Internal reference:TMS (tetramethylsilane)

FIGURE III. NMR Spectra of 4'-Nitro-4 Methoxy-α-Methylstilbene (Trans Isomer)
Irradiated with Duroquinone as the Sensitizer

Solvent:C_6D_6 98 atom %.D
Internal reference:Tetramethylsilane
60 MHz Spectra

200-300 C at 6°/min. The cis compound has a retention time of eight minutes while the trans appears after 13 minutes.

The primary disadvantage of this technique is the potential for thermal isomerization or decomposition. cis- and trans-α-Methylstilbene do not show evidence of decomposition or isomerization. However, the cis-4'-methoxy derivative is known to isomerize on standing at room temperature. No other isomer pairs have been analyzed to date.

Gel Permeation Chromatography. This technique is nondestructive and unlikely to cause isomerization. However, it is a lengthy process and not well suited to high sample volume analyses. It will be particularly useful in later work for separating matrix material and sensitizers from the stilbenes before further analysis.

Refractive Index Determination

Once a pure cis-trans pair is obtained, the refractive indices of each isomer can be obtained on Battelle's Brice-Phoenix Differential Refractometer, Model BP-1000-V, which has been designed for the precise measurement of the difference in refractive index between a dilute solution and its solvent. The limiting sensitivity is about three units in the sixth decimal place of refractive index difference, while the range is 0.01 units. Differential instruments are superior to conventional refractometers not only in accuracy but also in simplicity of the temperature control. The cis-trans pair found with the highest refractive index difference will initially be used for further study. Because there may be a trade-off between refractive index difference of the isomers and the ease of the isomer interconversion, the compound studied initially will not necessarily prove to be the most appropriate when all factors are considered.

Because pure cis-trans pairs have not yet been obtained, an alternate procedure was used to obtain approximate values of the refractive index difference. This technique involves the sensitized or unsensitized photochemical partial conversion of the trans isomer to the cis in deuterobenzene solution. Conversion of up to 64% was realized. After determining the isomer ratio in the solution by nuclear magnetic resonance, the difference in refractive indices between the photoisomerized solution and a similar solution of pure trans was determined using the Brice-Phoenix Differential Refractometer. The isomer ratio could be plotted vs. refractive index, giving a straight line from which the difference of refractive indices between pure cis and pure trans could be extrapolated. Preliminary experiments indicate that the difference between the refractive indices of cis- and trans-4-methoxy-4′-nitro-α-methylstilbene is approximately an order of magnitude larger than that originally found for cis- and trans-α-methylstilbene. (See Battelle's report for NASA Contract No. NAS8-26672, subcontract No. 114197 for a discussion of refractive index requirements) This implies a similar increase in sensitivity of a holographic system using such materials, and strongly supports the original assertion that the refractive index difference of isomeric stilbenes could be increased by increasing electron conjugation, and thus polarizability, in the trans isomer.

Photochemistry

The photochemical intraconversion of cis- and trans-4-methoxy-4′-nitro-α-methylstilbene has been studied only in a preliminary manner. Both sensitized and unsensitized isomerizations have been effected, although no attempt has as yet been made to quantify or optimize the photochemistry. The sole purposes to date were to demonstrate interconvertibility and to obtain isomer mixtures for refractive index measurements as described previously. The trans isomer can,

for example, be converted to cis by irradiation of a deuterobenzene solution with light of wavelength 360 nm and longer (trans-4-methoxy-4'-nitro-γ-methylstilbene absorbs with a maximum at 350 nm but tails to considerably longer wavelength). The return reaction, cis- to trans, was accomplished with 300 nm light.

 The cis/trans ratio obtained photochemically is a complex function of the triplet energy of the sensitizer and which at present must be determined experimentally. It is preferable to use sensitizers rather than to excite the isomer directly since the former course generally allows the use of more readily available wavelengths than those required for direct excitation.

 The following sensitizers were investigated briefly for use in the photoisomerization. Polychromatic light was used, however, and the steady state isomer ratio obtained contained about 20% cis in all cases, suggesting that the efficiencies of the self-sensitized reactions were quite high. These experiments must be repeated with monochromatic light corresponding to the absorption maximum for each sensitizer.

Acetophenone	α-naphthylphenylketone
Acridine	β-naphthylphenylketone
anthraquinone	Perylen
benzil	Pyrene
benzophenone	tetracyanoethylene
p-benzoquinone	
benz[α]anthracene	
4,4'-bis(dimethylamino)benzophenone	
9,10-dibromoanthracene	
9,10-dimethylanthracene	
dicyanomethylene-2,4,7-trinitrofluorene	
duroquinone	
Eosin Y	
9-Fluorenone	

LiNbO$_3$ STUDIES

Apparatus

An experimental system has been assembled to facilitate the study of the holographic recording behavior of doped LiNbO$_3$ and other potential memory materials. The apparatus was designed to facilitate the selection of spatial frequencies, polarization orientation, and power densities for the experiments. Provision was included for simultaneous playback of the grating during recording. An argon-ion laser was used as a source of write and erase radiation. It was fitted with a prism resonator which permitted a quick selection of output wavelength. The laser used has an output of more than 1 watt in each of the two strongest output wavelengths, 488.0 nm (cyan) and 514.5 nm (green). The output is linearly polarized with the electric vector in a vertical plane. A halfwave plate can be used to rotate plane of polarization so that the effect of polarization orientation can be studied. The bulk of the equipment shown in Figure IV is mounted on a large, seismically-isolated, granite optical table. This includes a rotating disc with a graded metal coating which is used for the overall beam intensity control. A system of mirrors then directs the beam onto another variable beam splitter where it is divided into two equal intensity beams. These beams each strike mirrors on the end of arms pivoted about the sample position. These mirrors direct the beams so that they converge onto the sample forming a sinusoidal diffraction grating within the material. Since the beams are planar and propagate horizontally, the grating is linear and vertical. In a transparent material such as the LiNbO$_3$ used in these studies, the grating structure exists in depth in the recording material. Since the beams are adjusted so that the bisector of the angle between the beams is normal to the recording surface, the grating structure exists as parallel planes that are not only vertical but are perpendicular to the front surface of the recording material.

Variable
Attenuator

Halfwave
Plate

Mirror

Argon-Ion Laser
with Prism Wavelength
Selector

Light
Trap

Mirror

Variable Ratio
Beamsplitter

He-Ne
Laser

Mirror

Mirror

Doped LiNbO$_3$
Wafer Specimens

x - y
Translation
stage

Diffracted
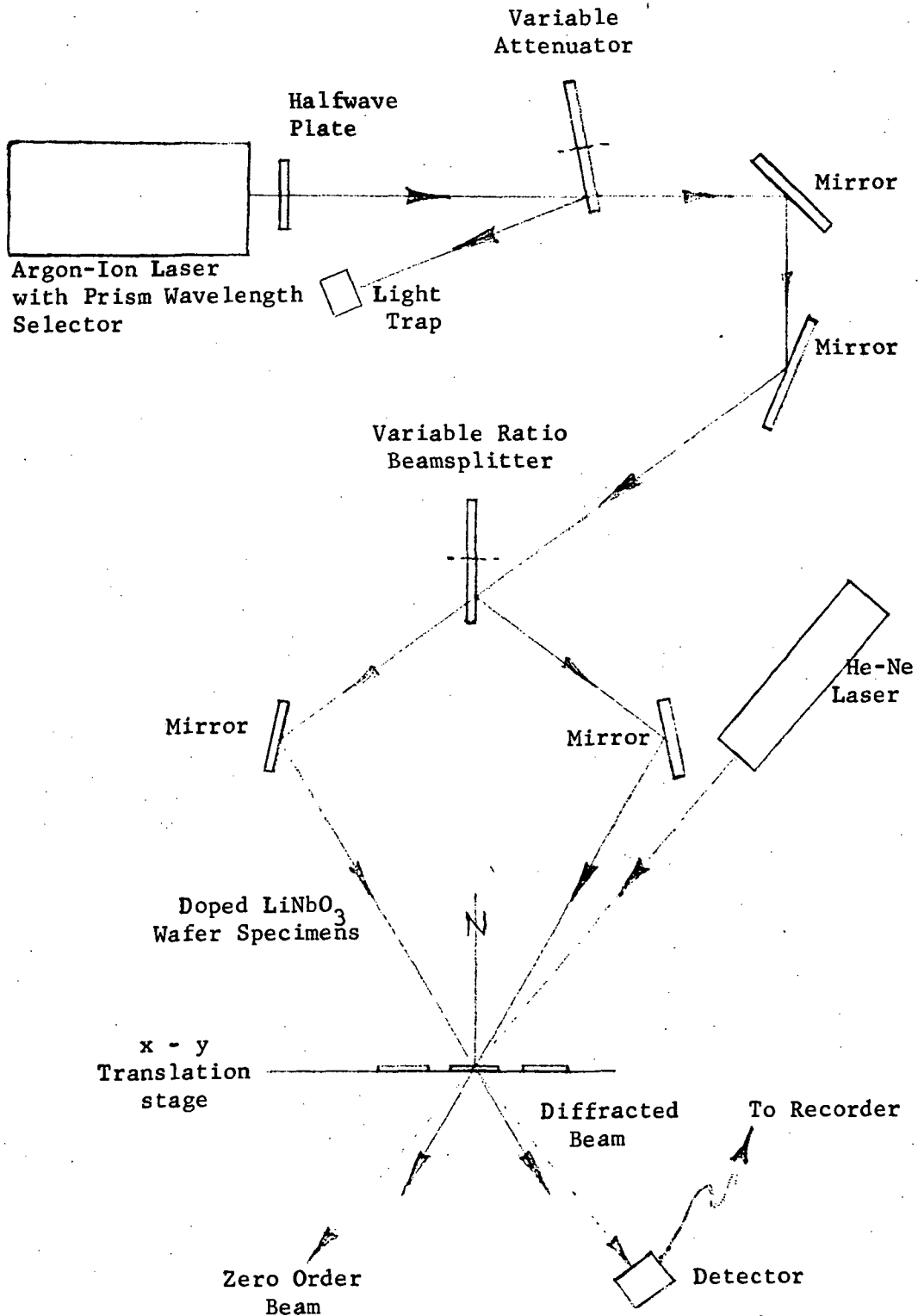Beam

To Recorder

Zero Order
Beam

Detector

FIGURE IV

Experimental arrangement for real time study of holographic recording.

The gratings are read with a 6238Å beam from a He-Ne laser. Use of a laser for the read function which has a different wavelength from the writing beam facilitates monitoring the grating during the writing process. However, since the samples used in these experiments were 1 mm thick, they exhibit a very strong Bragg effect. As a consequence, the playout (using a He-Ne laser) at a wavelength other than that used for recording requires careful angular alignment of the read beam in order to optimize the diffracted intensity.

The wafer specimens were mounted on an x - y translation stage with their c-axes horizontal and perpendicular to the planes of the diffraction grating. The stage was used to move the different wafers into the recording location and to permit selecting different areas of each wafer for exposure to the recording beams.

Samples

The $LiNbO_3$ samples used in this work were obtained from Crystal Technology Inc. of Mountain View, California. A total of three samples were used, doped with 0.010% Fe, 0.1% Fe and 0.1% Fe/0.05% Mo respectively. The samples measured 1 mm x 10 mm x 10 mm and were cut so that the symmetry axis lay parallel to the broad faces.

Observations

Dynamics of the Writing Process.   Using the apparatus described in
the preceding section, a number of observations of the time dependence of the
growth of the intensity of the diffracted red (633 nm) beam were made.   A typ-
ical set of data is shown in Figures V to VIII.   In taking these data, care was
exercised to keep the 488 nm writing power constant and to use the same area of
the sample for all measurements.   The data shown were taken in the order pre-
sented during a single day.   In each case, care was taken to align the He-Ne read
beam to maximize the intensity in the diffracted beam.   It was always possible
to obtain diffraction efficiencies of greater than 30%, even though $\Delta\theta$, the
angular acceptance of the grating is as small as 0.25 mrad.

In each of the sets of data presented in Figures V and VIII, the mater-
ial was erased between runs by exposure to the green output of the argon-ion
laser.   As can be seen, the general shape of the efficiency vs time curves is
the same in each run.   Changing the grating spacing by changing the angle of the
writing beam did not produce any clearly defined change in the slope of the
curves.   The most noticeable trend is a continuing increase in writing efficiency
as the material is recycled.

We also observed what might be described as an increase in smoothness
of the data as the material was cyclically erased and rewritten.   In "new"
material there are noticeable and frequent fluctuations in the scatter as well
as rapid and anomalous increases and decreases in diffraction efficiency during
writing.   These tend toward smaller amplitude and become less frequent as the
material is reused.   These observations, which have not, to our knowledge, been
previously reported, might be of considerable practical importance.

FIGURE V

Diffraction efficiency vs. exposure 0.1% Fe in LiNbO₃.

Incident power density 58 mW/mm²

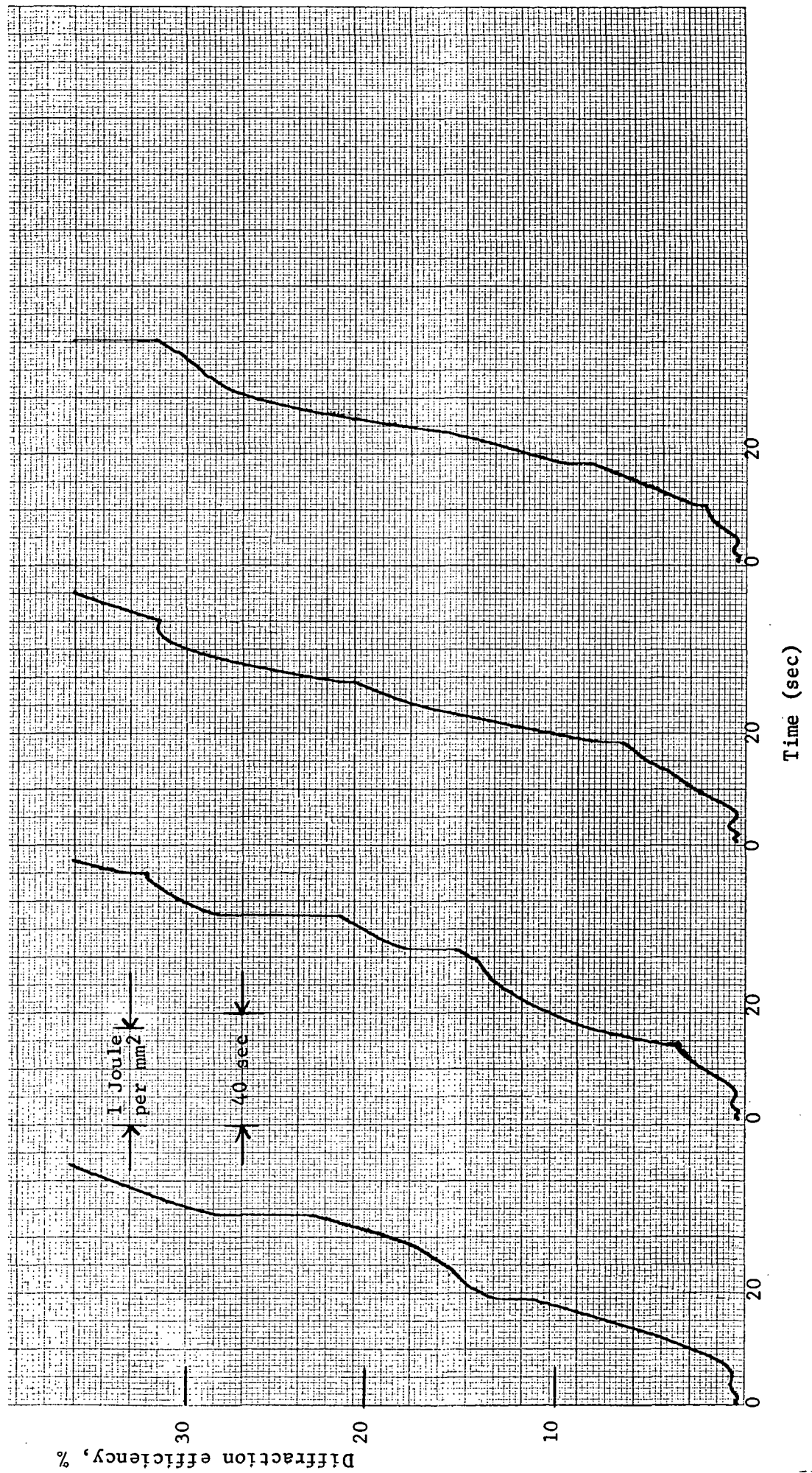Grating spacing 2050 lines pairs/mm.

FIGURE VI

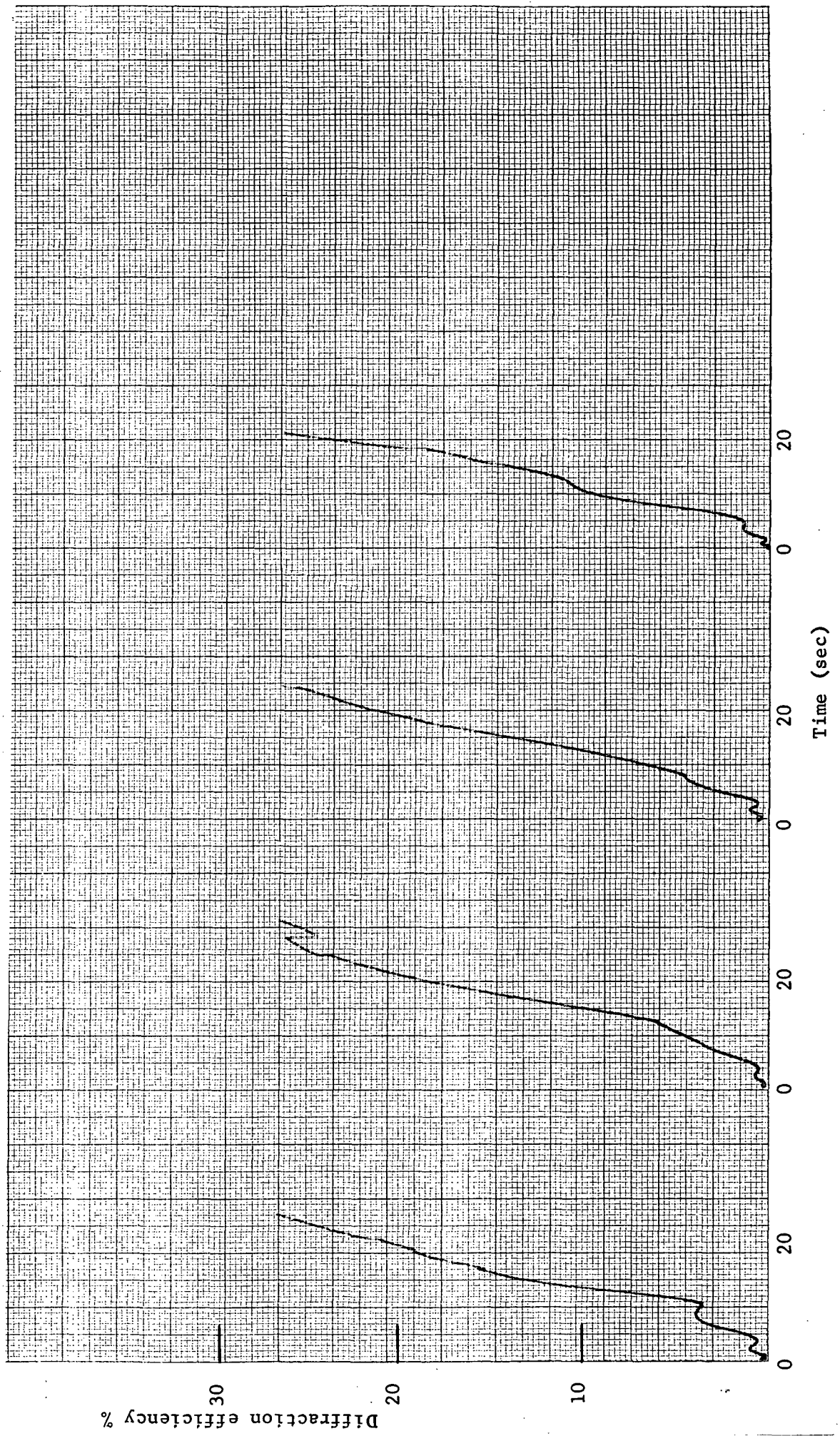Grating spacing 1060 line pairs/mm.
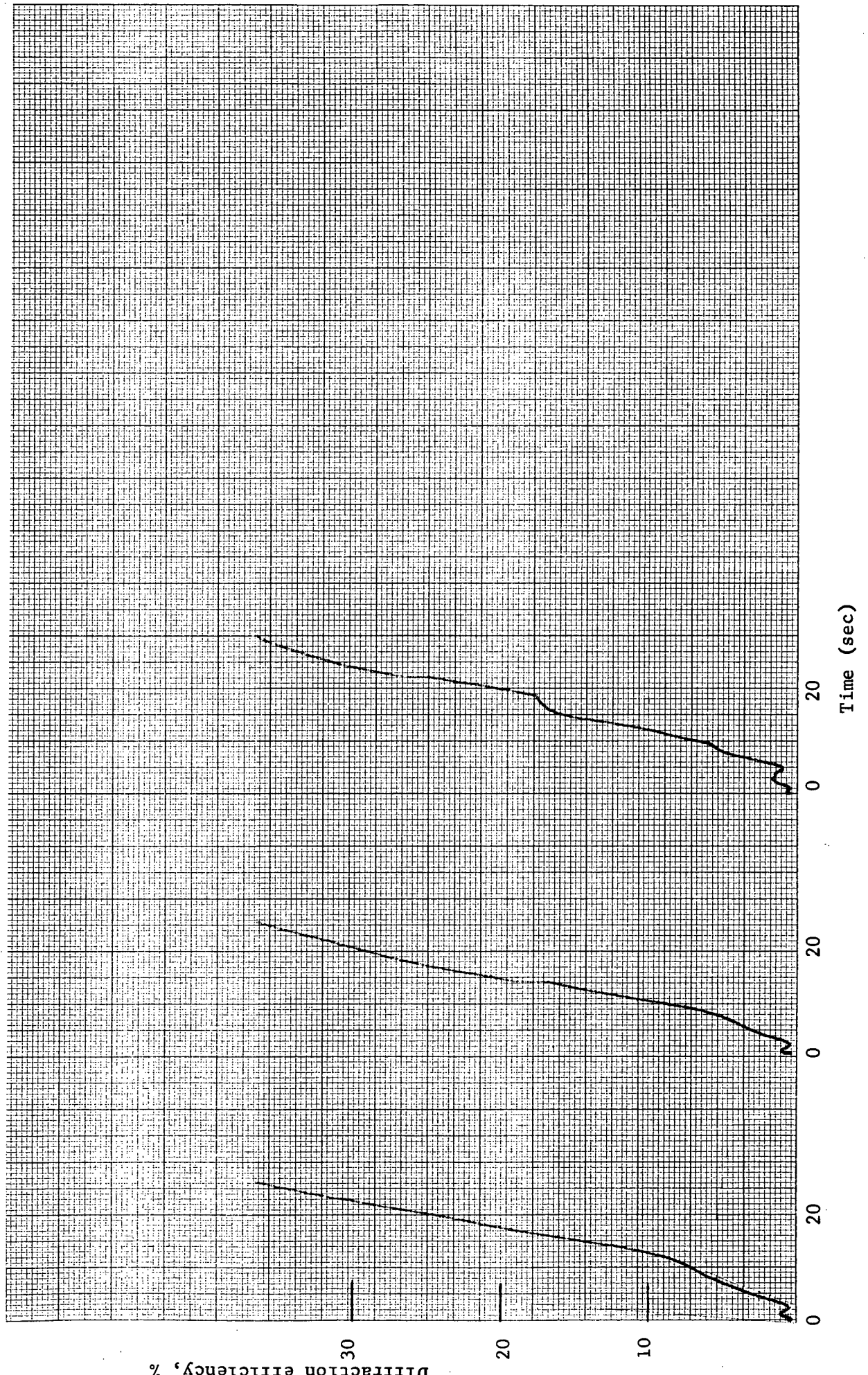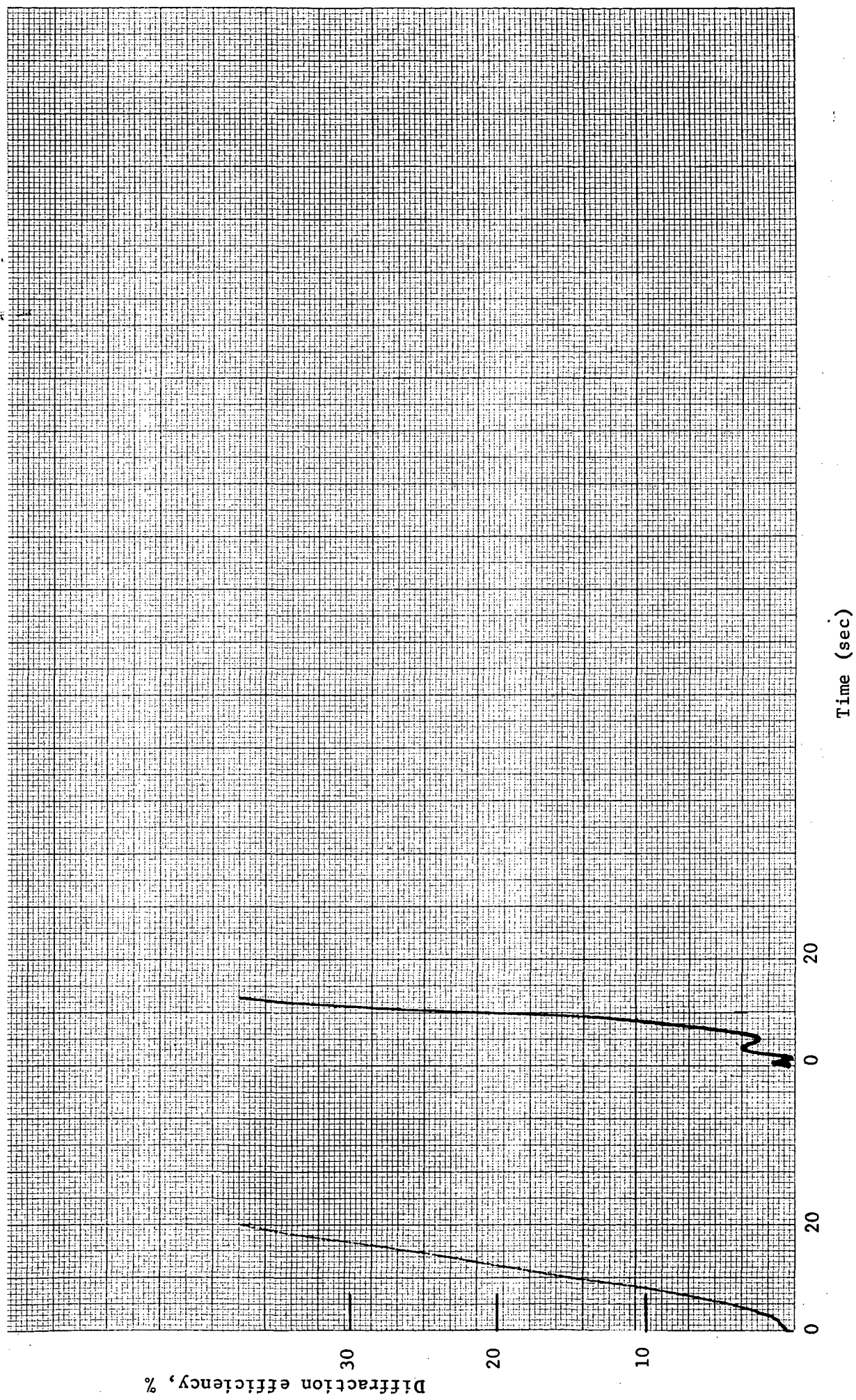
FIGURE VII

Grating spacing 2050 line pairs/mm.

FIGURE VIII
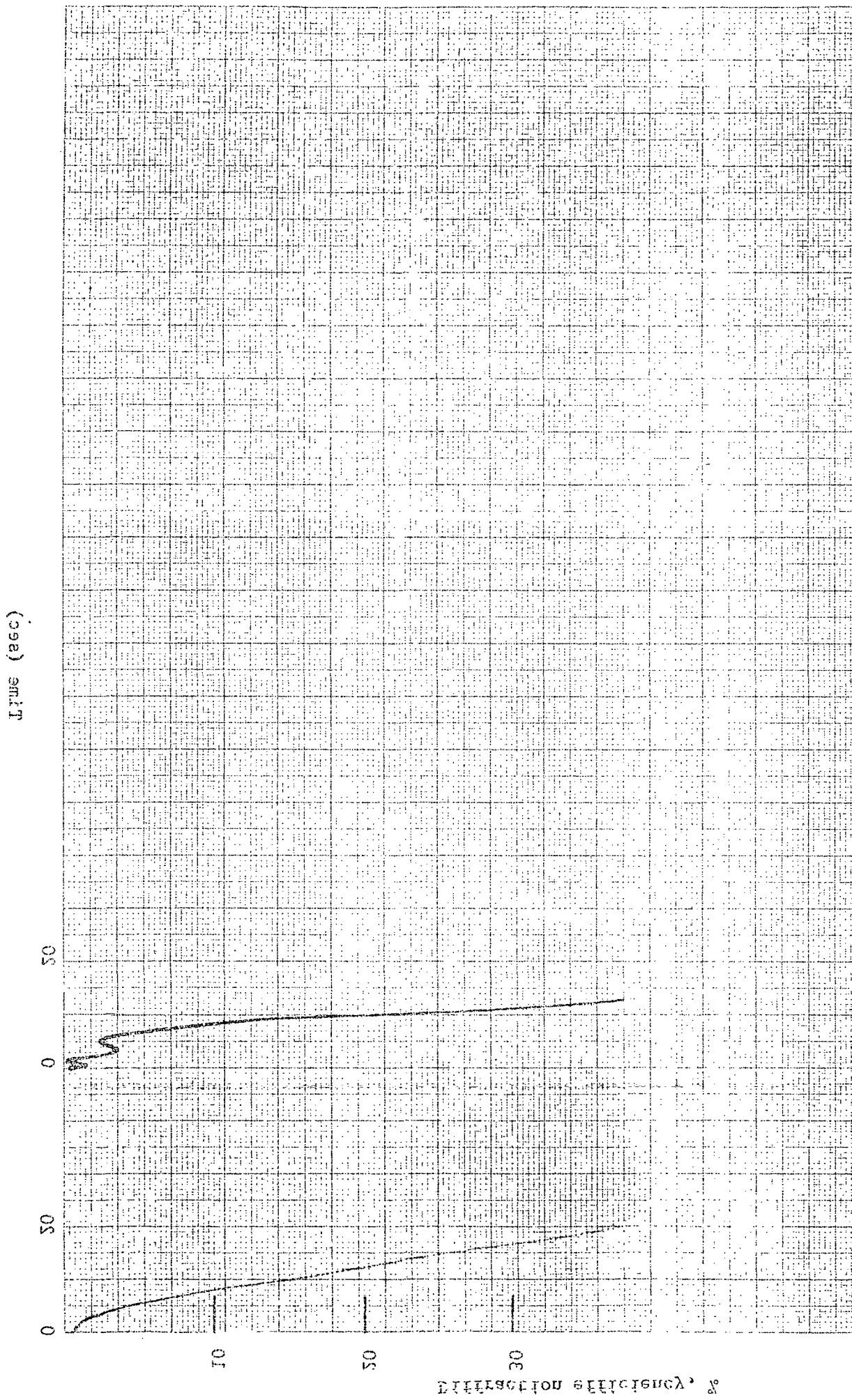
Grating spacing 1060 line pairs/mm.

Diffraction efficiency, %

Time (sec)

Time (sec).

Grating spacing 1000 line pairs/mm.

FIGURE VIII

Diffraction efficiency, %

10

20

30

The grating spacing was varied by a factor of two from 1060 to 2050 lines/mm. One might expect that with a larger grating spacing, the time required to reach saturation in diffraction efficiency would be increased and the initial rate of "grating production" decreased because of the larger index of refraction change required and the greater average distance a photoelectron would have to diffuse before it is finally trapped. These effects were not observed, possibly being overshadowed by the increase in slope occurring on erasing and rerecording regardless of the grating spacing. Further experiments to determine the factors controlling the increcrease in sensitivity on recycling to find the number of cycles after which this sensitivity increase saturates under various physical conditions, to see whether the grating spacing effects can be demonstrated after the recording sensitivity has reached its limit, and to determine the sources of the fluctuations in sensitivity observed in recording in new material would clearly be desirable.

Theoretical Considerations

The present contract provided partial support for a theoretical study of the writing process in $LiNbO_3$. The main thrust of this work was to consolidate some of the existing theoretical work in the field with particular attention being paid to the physical conditions under which the theory should be valid. Among the theoretical descriptions of the "optical damage" process by which phase holograms are recorded are those of Johnston and Amodei. A short paper discussing certain points concerning the conditions for validity of these theories was prepared and is included here as an appendix.

APPENDIX I

OPTICAL DAMAGE AND INTERNAL FIELDS IN PYROELECTRICS

by

Van E. Wood

The nature of the optical damage mechanisms in ferroelectrics such as $LiNbO_3$ has engendered considerable discussion, stimulated in large measure by the possible application of such materials to the storage of phase holograms. In one of the best-known papers on this subject, Johnston[1] proposed that drift of photoexcited carriers in the electric field resulting from the polarization variation due to the changed nature of the donor sites, followed by retrapping in the less illuminated region in such a way as to negate the internal electric field variations, could lead to polarization variations sufficient to explain observed electrooptic effects. Subsequently Amodei, in a number of papers,[2] emphasized the importance of diffusion of photoexcited carriers and suggested that the electric field of the retrapped carriers could be responsible for the electrooptic effects. Staebler and Amodei[3] have recently presented experimental evidence indicating that diffusive processes play a sig-nificant role in undoped $LiNbO_3$, while Auston and Glass[4] have shown that excitation (not, as it happens, ionization) of impurities can lead to sizable polarization changes in $LiTaO_3$ and $LiNbO_3$. It is of course clear that different effects may be primarily responsible for damage production in different materials or in materials with different dopants [3,5]. In the present note we define explicitly the physical conditions to be met if either model is to be valid, and suggest the synthesis of theoretical

ideas which will eventually be required for critical appraisal of
experimental data. We do not attempt here a complete dynamic analysis;
this would be of little value until quantitative data on the nature of
the traps and the properties of the carriers are available. Some
acquaintance on the part of the reader with the first two references
will be assumed. In common with the other authors, we do not take
any account of the dielectric nonlinearity. Also, the possibility of
large-scale frozen-in fields[6,1,2] will not be discussed.

Let us consider a pyroelectric with a unique polar axis in which
initially the constant electric field arising from the uniform polari-
zation is cancelled by surface charges. We suppose that as in Johnston's
model there are both photoionizable donors and traps for free carriers,
and that a space-charge ρ_{sp} and an induced polarization P varying along
the polar (χ-) axis may be produced upon non-uniform illumination of the
sample. Consider that some such process of illumination has been
carried out, and that the light has been turned off and the photoelectrons
retrapped. Then in general the electric field at the point χ is given
by[7]

$$E(\chi) = \frac{1}{\epsilon_o}\left[\int_0^{\chi} \left(\rho_{sp}(\chi') - \frac{dP}{d\chi'}\right) d\chi' - \frac{1}{\ell} \int_0^{\ell} (\ell - \chi') \left(\rho_{sp}(\chi') - \frac{dP}{d\chi'}\right) d\chi'\right] \quad (1)$$

where the sample extends between zero and ℓ along the polar axis and ϵ_o
is the static dielectric constant. (Small spatial variations in ϵ_o will
be ignored.)

Eq. (1) may be rewritten

$$E(\chi) = \frac{1}{\epsilon_o} \left[\bar{P} + \bar{P}_i - P(\chi) - \int_x^\ell \rho_{sp}(\chi') \, d\chi' \right] \quad , \quad (2)$$

where $\ell \bar{P} = \int_o^\ell P(\chi) \, d\chi$ and $\ell \bar{P}_i = \int_o^\ell \chi \, \rho_{sp} \, d\chi$. It is assumed by Johnston that the final configuration of retrapped carriers is such that $E(\chi) = 0$ for any χ. If this is to be the situation, then upon differentiating (2) we find

$$dP/d\chi = \rho_{sp}(\chi) \quad \text{(all } \chi \text{ inside sample)} \quad . \quad (3)$$

Johnston's corresponding Eq. 2.4 has an extraneous factor $(\epsilon-1)$ on the right side. Eq. 3 provides a necessary, but not quite a sufficient, condition for $E(\chi)$ to be zero everywhere. If we assume further that there are no leftover free carriers, that there are no interactions (direct or indirect) among the defects, and that there are no multiple donors or traps, then we can write

$$\rho_{sp}(\chi) = \rho_+(\chi) + \rho_-(\chi) \quad (4)$$

where ρ_+ and ρ_- are respectively the charge densities of charged donors and filled traps, and also

$$P(\chi) = a \, \rho_+(\chi) + b \, \rho_-(\chi) \quad (4b)$$

where a and b are simply constants. Then (3) would require that

$$\rho_{sp} = a \frac{d\rho+}{d\chi} + b \frac{d\rho-}{d\chi}$$

Inserting this expression for ρ_{sp} into Eq (2) and performing a number of
integrations by parts, we find that $E(\chi)$ is indeed zero everywhere; so
under these conditions (which should be realizable), (3) is both necessary
and sufficient for the electric field to vanish. This result is independent
of the magnitudes of a and b. Thus if (3) and (4b) hold, and possibly
under some other conditions, a situation in which E = 0 may be attained.
Furthermore, this configuration is surely that of lowest free energy
(neglecting rearrangement entropies), since it corresponds to dU/dP = 0.
But a system with charged traps does not necessarily reach this configur-
ation under arbitrary patterns of carrier excitation or for arbitrary
carrier dynamics.

Amodei[2] has given what amounts to one simple example of this
failure to reach the E = 0 configuration using sinusoidal excitation, a
long light pulse, and fast trapping. He does not explicitly separate the
electric field into contributions from donor ions and retrapped electrons
and he considers polarization changes to be negligible; otherwise his model
is similar to Johnston's. He calculates the steady-state internal field
to be expected and shows that it can be large enough to account for observed
electrooptic effects. The steady state in this situation is the condition
of no further photocurrent flow, rather than that of no internal electric
field. The experimental evidence is strong that, at least in $LiNbO_3$, it
is the former condition that occurs.[3,8] The dynamics of the optical
damage process and the pattern of excitation again must be the factors
responsible for this. Unfortunately, the simple one-dimensional model
discussed so far, while satisfactory for calculating the steady-state field,
is not in general adequate for describing the dynamics since the long-range

electric fields arising from plane sheets of donor charges act to inhibit strongly the initial redistribution of photocarriers by diffusion.

One may convince oneself of this by working through examples,[9] but as even the simplest examples are rather complicated, we shall not pursue this. There is no physical difficulty here, however, since the distance necessary to diffuse before retrapping to form a grating may be comparable with the mean impurity spacing; so the field seen by a diffusing charge carrier may be more like that of a single ion, even near the end of the writing process. Other factors that may need to be considered include the energy distribution of the carriers[8] and effects of dark carriers[10] as well as the polarization effects of Johnston.[1]

Internal electric fields in inhomogeneous ferroelectrics influence the observed electrooptic effects in the same way the polarization does. Since the light-wave field is small, the electrooptic effects at a given point in the material may be considered theoretically as a thermodynamic perturbation about the local quasi-equilibrium state. The phenomenological description[11] of such effects involves expansion of the elements of the optical indicatrix in powers of the local electric displacement $D = \epsilon E + P$, rather than the polarization P. In Johnston's paper,[1] this distinction is not made since D and P are there equal by hypothesis.

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